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<b>(54) Title:</b> PROCESS FOR PRODUCTION OF ZEOLITES FROM RAW MATERIALS CONTAINING ALKALI ALUMINO HYDRO-SILICATES  <b>(57) Abstract</b>  The invention relates to a process for production of zeolites from raw materials with alkali alumino-hydrosilicate content comprising converting the alkali alumino-hydrosilicate content of the raw material into an amorphous state by acidic treatment, separating the intermediate amorphous solid material from the liquid phase and optionally purifying same, re-suspending it in water, alkalizing the suspension, followed by forming a slurry of the composition corresponding to the type of zeolite to be manufactured optionally by blending it with components containing SiO <sub>2</sub> , and/or Al <sub>2</sub> O <sub>3</sub> and/or Na <sub>2</sub> O, followed by crystallization by method known per se after optionally adding crystal nuclei and/or aging of the synthesis slurry and separating the obtained zeolite product.		

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**Process for production of zeolites from raw materials containing alkali  
alumino hydro-silicates**

Technical Field

5       The invention relates to a process for production of zeolites from raw materials containing alkali alumino-hydrosilicates.

Background Art

10       The processes which are based on processing materials containing alkali alumino-hydrosilicates, first of all by-products of various industries are more and more important from the economical point of view. A process is known e.g. for manufacturing 4A zeolite from "red mud" obtained from the Bayer process which is widely used for making alumina from bauxites [Cardile C.M.: Removal and conversion of DSP in Red Mud to type 4A Zeolite (Int. Bauxite Tailing Workshop, 15 1992)]. The core of the process is the separation of particles smaller than 45  $\mu\text{m}$  consisting mostly of alkali alumino-hydrosilicate with cyclones from particles greater than 45  $\mu\text{m}$ , which consist mostly of  $\text{Fe}_2\text{O}_3$ . The alkalinity of the < 45  $\mu\text{m}$  fraction is reduced by washing with water, subsequently the slurry is acidified to  $\text{pH} \approx 6.2$  using  $\text{H}_2\text{SO}_4$  and the Ca- and Mg-salts are removed by filtration or 20 decantation. The filtrate is further acidified to  $\text{pH} \approx 2.3$  in order to bring the silicate components into a relatively stable colloid-like solution. The alumina containing silica solution obtained in this way is separated from the residues of red mud and is subsequently treated with the necessary amount of NaOH. Subsequently NaA zeolite is crystallized. The NaA (LTA) product is washed to remove the mother 25 liquor (to below a value of  $\text{pH} 10.5$ ) and dried. The filtrate mother liquor contains alkali sulfates in fairly high concentrations, from which the alkali content can partly be recovered by treatment with slaked lime (causticisation) and subsequently utilised in the Bayer process. In case of causticisation with slaked lime the alkali recovery yield is low, in fact, it is less than 50%. The recovered alkali solution 30 contains non-reacted lime particles (and some calcium sulfate), consequently, the utilization of the solution obtained from the causticisation has little relevance in the alumina manufacturing process. One great disadvantage of the process

described here is that a significant amount of sulfuric acid is required to acidify the raw material to a solution of pH 2.3 and a substantial amount of sodium hydroxide is needed for neutralization and converting the slurry alkaline with a pH of greater than 13.5 that is needed for the crystallization. A further disadvantage is that the iron oxide content of the red mud at least partly dissolves at pH 2.3 and thereby the zeolite product becomes contaminated. Therefore the commercial application of this process is not profitable and the purity of the product does not reach the European Standards.

10 The WO 91/15427 A1 patent application document laid available for the public describes a process in which sodalite or cancrinite originating from the Bayer alumina manufacturing process is used as it is or together with red mud; the sodium alumino-hydrosilicates content is dissolved with diluted sulfuric acid, subsequently a precursor gel is made from the resulting solution by blending it with a sodium hydroxide or sodium aluminate solution at a pH greater than 12, usually at a pH of 13.5. The precursor gel is aged at a temperature of 70-95°C and subsequently NaA zeolite is obtained by crystallization. This process is basically identical with the process described above and the disadvantages are similar as well. It is to be emphasized that the viscosity temporarily increases to a great extent when the pH of the acidic solution is gradually increased. In order to avoid this kind of difficulty with mixing, it was proposed that all the amount of alkali which is needed to form the precursor be added within a very short time period. Inverse blending was also proposed (i.e. the acidic sodalite solution is to be added to the sodium hydroxide or sodium aluminate solution so that the difficulties with mixing be eliminated).

There is a need to develop such a process by which zeolite(s) can be made from raw materials containing alkali alumino-hydrosilicate in which the acid and alkali consumption are moderate, the zeolite product(s) has/have such a purity which meet(s) the expectations of the users in the world market, and the synthesis of zeolite can be carried out in common industrial equipment.

### Disclosure of Invention

In our investigations it was found that a precursor slurry that is suitable for the crystallization of zeolite can be directly formed from alkali aluminohydrosilicates provided that the alkali aluminohydrosilicates are transformed to an amorphous state by an appropriate acid treatment. In this case the crystalline structure of the alkali aluminohydrosilicates is destroyed by the removal of the charge compensating (mainly  $\text{Na}^+$ ) cations. In order to reach this goal considerably less (sulfuric) acid is needed than for completely dissolving the alkali aluminohydrosilicate. Furthermore, the process steps of dissolving the raw material in the acid and of making a strongly alkaline solution again from the highly acidic solution can be avoided. The gel formation, which is a difficult step of the previous processes can also be avoided since as per our invention, the precursor slurry, suitable for crystallization of zeolite can be obtained by blending the amorphous alkali aluminohydrosilicates with silica, alkali and alumina in appropriate amounts. The amorphous solid zeolite precursor can be washed free of the excess acid or even dried. After addition of (considerably less) sodium hydroxide (and other components) the slurry obtained (possibly after aging) is ready to be crystallized into various commodity zeolite products (like NaA, NaX, NaY or maximum aluminium P zeolite).

On the basis of this understanding, this invention provides an improved process for the transformation of alkali (preferably sodium) aluminohydrosilicates into various zeolites by acid treatment to destroy their crystalline structure first, (an amorphous material is made in this way), followed possibly by purification, and a subsequent separation of the intermediate amorphous solid from the liquid phase; then the slurry for zeolite crystallization is prepared from this amorphous material by suspending it in water which possibly contains alkali (sodium hydroxide) and possibly after addition of alumina-, and/or silica- and/or  $\text{Na}_2\text{O}$ -containing components and/or crystallization promoters thereby adjusting the

proper zeolite slurry composition. The zeolite slurry is possibly aged and/or blended with zeolite nuclei. After these the crystallization, filtration and/or washing and drying are carried out according to the known processes.

5        According to the present invention, natural alkali alumino-hydrosilicates and/or industrial by-products or wastes containing mainly alkali alumino-hydrosilicates can be used as raw materials. Materials with at least 50w% (on dry basis) alkali alumino-hydrosilicates in the form of crystalline or amorphous compounds are considered as raw materials. Further on materials with alkali  
10        alumino-hydrosilicate content as defined here are considered as raw materials.

Acceptable raw materials are the desilication products which are obtained in the first step of the desilication of the pregnant liquor that is carried out at 150-170 °C in the sintering alumina manufacturing process. Natural materials which  
15        contain alkali alumino-hydrosilicates such as nepheline with a low iron content can be used as raw material, too.

It is to be mentioned that "sodium alumino-hydrosilicate" materials of high purity can preferably be obtained from the Bayer alumina manufacturing process  
20        by an Improved Low Temperature Digestion Process [Gy. Bánvölgyi: Travaux Vol. 24, 1997 (No 28) ICSOBA, Budapest, Proc. of 8th International Congress, April 16-18, 1997, Milan, Italy, pp 214-228] or in combined Bayer/sintering processes.

The raw materials, which can be used in the embodiment of this invention,  
25        are desilication products of sodium alumino-hydrosilicate type originating from various alumina manufacturing processes or scales deposited therein, as they are available, cheap and materials otherwise difficult to utilize.

The various alkali alumino-hydrosilicate by-products of the alumina  
30        manufacturing processes can be described with the following general formula



where  $0 \leq k \leq 2$ , and X means  $2\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $2\text{Cl}^-$ , or  $2\text{Al}(\text{OH})_4^-$ . If crystalline, their crystal structure is either that of sodalite (Bayer sodalite), nosean, or cancrinite (the latter is formed during the high temperature digestion of bauxites, or in scalings that are formed in low temperature digestion autoclaves during very long time periods).

The embodiment of the process described in this invention is not restricted to those raw materials mentioned previously as examples, neither in their chemical composition, nor in their crystalline structure.

As mentioned previously, the basic idea of the present invention is that the alkali alumino-hydrosilicate raw material is not dissolved in the acid, it is only transformed to the amorphous state by exchanging the charge compensating alkali (mainly  $\text{Na}^+$ ) ions for  $\text{H}^+/\text{H}_3\text{O}^+$  ions. This causes a very rapid collapse of the crystal structure even at room temperature. For this, a little more acid (10-30% in excess) is needed than that required only to neutralize the overall alkalinity of the raw material, nevertheless, this amount of acid is still less than half of the one that is to be used for the complete dissolution of the alkali alumino-hydrosilicates at  $\text{pH} \approx 2.3$ . From the chemical character of the treatment it is obvious, that the concentration of the acid is irrelevant, the ion exchange takes place even in weak acid solutions. The structural aluminium is left intact, therefore the exact amount (and concentration) of the acid should be determined experimentally. The collapse of the crystal structure can easily be tested by X-ray diffractometry. The material is amorphous if the acid-treated, filtered and washed sample after its drying and treatment at  $\sim 600^\circ\text{C}$  for 1-2 h, the X-ray pattern that is characteristic to the alkali alumino-hydrosilicate of the raw material substantially disappears and the X-ray pattern is characteristic of the amorphous material.

The acid that is used for the treatment can be any mineral or organic acid, a mixture of various acids, it can be an acidic waste from the industry, such as from

alumina refineries, which may contain solid and/or dissolved silica-containing scalings from the acidic cleaning of the equipment. Preferred is a sulfuric acid solution of 3-60w%.

5        In order to be sure that the crystal structure of the alkali aluminohydrosilicate has collapsed, i.e. the material has become amorphous, the temperature of the acid treatment should be between 20 and 160 °C, preferably at 60-80 °C.

10        The product of the acid treatment can be filtered off from the slightly acidic (pH  $\approx$  4.5-5) solution without difficulty, and if necessary, the excess acid can be removed by washing and later on it can be neutralised with diluted alkali. If iron impurities are present, their complexation can be carried out preferably in the acidic solution. The washed (neutralised) zeolite precursor can be dried and  
15        stored if the further processing steps shall be carried out afterwards.

According to the present invention the next step of converting the precursor to zeolite product is the preparation of the synthesis slurry from the amorphous intermediate material/product. The composition of the synthesis slurry depends on  
20        the type of zeolite to be made. Water glass (sodium silicate) solution is preferably used as SiO<sub>2</sub> source. The water glass, which is commercially available usually, does not need to be purified. The same is relevant for the sodium hydroxide, irrespective of whether it is solid or in solution. The sodium hydroxide solution should not contain more than 10% of sodium carbonate. In alumina refineries  
25        spent liquor is mostly used as Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O source. The carbonate content of the spent liquor should not be more than 10% of the total alkali content otherwise the prescriptions should be modified (e.g. lower temperature is to be applied) in order to eliminate the "carbonate effect". Of course, other SiO<sub>2</sub>, Na<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> sources can also be used in the zeolite synthesis, however their price is usually  
30        far too high to be competitive with spent liquors or wastes and/or by-products of the alumina refineries.



No gel-formation is to be applied in the invention disclosed here, therefore the sequence of admixing of the respective components is not important. On the other hand, very efficient (shear-)mixing should be used to reach maximum  
5 homogeneity of the slurry and it is most often a must to maintain vigorous mixing even during the synthesis, except for certain zeolite products where such vigorous mixing is prohibited, as in the synthesis of NaY.

In some cases crystallisation of the expected zeolite is possible only after  
10 appropriate ageing of the slurry, or addition of crystal nuclei. Types NaA and NaX or even NaP<sub>6</sub> (if the Si/Al ratio is greater than 3 and K<sup>+</sup> ions are present in the slurry) crystallise spontaneously, therefore, no crystal nuclei addition is necessary. On the contrary, NaY can only be produced if (NaX) nuclei are added to the slurry before crystallisation. NaX can be prepared in mixed slurries if  
15 crystallisation is preceded by 4-6 h ageing at about 40-60 °C.

Crystallisation, as usual in the industries, is carried out in the 60-170 °C temperature range, depending on the type of zeolite. NaA(LTA) can be produced in excellent purity between 60-88 °C, whereas making NaP<sub>6</sub>(GIS) zeolite needs  
20 higher, preferably 110-135 °C temperature. Mixing, preferably vigorous mixing is generally advantageous. Nevertheless when mixing influences the type of zeolite that forms, no mixing is recommended, or the necessary amount of nuclei should be added before the start of the crystallisation with mixing.

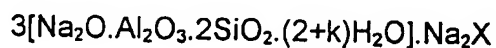
25 The time of crystallisation lasts from 0.5 h to several days, depending on the type of zeolite and the crystallisation temperature. Generally, the commercially important types with high specific surface area and open pore structure are all metastable from the physico-chemical (thermodynamical) point of view, therefore, extended heating may cause their transformation into stable type(s) which have  
30 compact structures and have no practical commercial use.

Filtration and washing until the pH of the filtrate decreases to 10.5 or less follows the crystallization. The filter cake is dried at 100-120 °C.

The previously mentioned zeolite types, NaA (LTA), NaX (FAU), MAP-  
5 NaP<sub>6</sub>(GIS) have found several application as detergent builders, desiccants, adsorbents, and carriers for perfumes, animal nutrients or catalysts.

The synthesis procedure described in the present invention allows the production of a wide variety of zeolites from natural raw materials, industrial by-  
10 products and wastes as well. The present invention can be used for processing of the desilication by-product (sodalite) of the pregnant liquor desilication of the alumina refineries.

The possibly negative environmental impact of the process according to the  
15 present invention is significantly less than that of the ones of the known processes mentioned in the introductory part. For example, when sodium aluminohydrosilicate corresponding to the formula



20

where  $k = 1$  and  $\text{X} = 2\text{OH}^-$  is dissolved (with dissolution of the sodium aluminohydrosilicate with sulfuric acid and proceeding with the dosage of the sulfuric acid until the pH reaches a value between 2 and 3) as indicated in the relevant patents WO 91/15427 A1, a significant amount of  $\text{Na}_2\text{SO}_4$  is generated  
25 which can hardly be disposed of in an environmentally sustainable manner. On the contrary, according to the present invention, less sulfuric acid is needed for the ion exchange, and thus less amount of sodium sulfate is generated. If the invention is implemented next to a Bayer alumina refinery, and the filtrate from the zeolite production that contains a certain amount of  $\text{Na}_2\text{SO}_4$  is used in the Bayer  
30 process, at least a part of the caustic make-up can be provided by this filtrate, since the desilication product can be obtained at least partly as sulfate-sodalite (nosean,  $\text{X} = \text{SO}_4^{2-}$ ) instead of hydroxi-sodalite. Thereby the sulfuric acid demand

for neutralization of the desilication product can further be reduced and even less sodium sulfate is formed in the zeolite production.

The "theoretical" (stoichiometric) sulfuric acid demand for the respective  
5 processes is shown in Table 1 as it follows:

Table 1

Raw materials and processes	H <sub>2</sub> SO <sub>4</sub> demand, moles for 1 mole formula- weight	H <sub>2</sub> SO <sub>4</sub> demand in kg-s for 1 t of raw material
raw material: hydroxide sodalite process: WO 91/15427 A1	13	1165
raw material: hydroxi-sodalite process: as per present invention	4	358
raw material: nosean process: as per present invention	3	254

The composition of the raw material and the process parameters influence  
10 the acid consumption that is really needed to carry out both processes. The  
figures given in Table 1 are based on the theoretical assumption that during the  
acid treatment according to the present invention only the charge compensating  
Na<sup>+</sup> ions should be replaced, while in the process of WO 91/15427 A1 both the  
Na- and the Al-contents of the alkali alumino-hydrosilicate have to be dissolved by  
15 the acid.

As far as it is shown in Table 1, as per the present invention, significantly  
less acid is demanded for the acid treatment, compared with the WO 91/15427 A1  
process. It should also be taken into consideration that in the WO 91/15427 A1  
20 process the pH has to be reduced to a value between 2 and 3 which further  
increases the acid consumption. In case of our process disclosed here a pH which

is only somewhat lower than the neutral is characteristic. It is also to be mentioned that the neutralization of the acidic solution with a pH between 2 and 3 needs some further amount of caustic, therefore more sodium sulfate is formed which increases the environmental concerns due to the disposal of the latter.

5

Tables 2 and 3 show further comparisons between the process as per the present invention and the process disclosed in WO 91/15427 A1. The "theoretical" sodium hydroxide consumption is shown in Table 2 and the "theoretical" sodium sulfate production in Table 3. (The data indicated in these  
10 tables are calculated on the same theoretical assumptions that has already been discussed in connection with Table 1.)

Table 2

Raw materials and processes	NaOH demand, moles for 1 mole formulaweight	NaOH demand in kg- s for 1 t of raw material
raw material: hydroxide sodalite process: WO 91/15427 A1	26	951
raw material: hydroxi-sodalite process: as per present invention	8	292
raw material: nosean process: as per present invention	8	277

15

Table 3

Raw materials and processes	Na <sub>2</sub> SO <sub>4</sub> production, moles for 1 mole formulaweight	Na <sub>2</sub> SO <sub>4</sub> production in kg-s for 1 t of raw material
raw material: hydroxide sodalite process: WO 91/15427 A1	13	1687
raw material: hydroxi-sodalite process: as per present invention	4	519
raw material: nosean process: as per present invention	3	491

As it is shown in Table 2 a substantial saving can be attained in the NaOH  
5 consumption, if the process according to the present invention is used. It is  
demonstrated in Table 3 that significantly less Na<sub>2</sub>SO<sub>4</sub> is produced with the  
present invention than with the known process.

Consequently, the process according to the present invention is superior to  
10 the previously known processes as far as the basic reagent consumptions and  
also the environmental disadvantages are concerned.

If the process according to the present invention is implemented in  
connection with an alumina refinery, the mother liquor of the zeolite synthesis that  
15 contains mainly NaOH and some sodium aluminate and some sodium sulfate can  
be fully utilized in the Bayer process as make-up caustic. Furthermore, the  
Na<sub>2</sub>SO<sub>4</sub> (which is obtained when the alkali alumino-hydrosilicate raw material is  
converted into an amorphous material) can be used in the alumina manufacturing  
process at least in part.

The process according to the present invention can also be used for processing hydroxide sodalite (or analcime) which can be formed if some trouble occurs with the zeolite synthesis process that is widely used for the time being.

5       The process according to the present invention is demonstrated by examples, however these examples shall not restrict the scope of the invention. Laboratory circumstances are shown in the following examples. The operations in the examples can be implemented in a commercial scale, in common industrial equipment after their scaling up which is a common task of a professional who  
10      has experience in the relevant field.

### Example 1

#### Making NaA zeolite from hydroxi-sodalite

100 g hydroxi-sodalite, with the composition of  $1.3\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$  is  
15      blended with 854.0 g of 5%  $\text{H}_2\text{SO}_4$  solution (this is a 10% excess relative to the amount of  $\text{H}_2\text{SO}_4$  that is stoichiometrically required to neutralize the alkali content) and the blend is mixed for 3 hours at  $60^\circ\text{C}$ . After this, the liquid phase, which contains sodium sulfate (and possibly Fe(III) sulfate in traces), is separated by filtration, the solid phase is washed once with distilled water and dried at  $110^\circ\text{C}$ .  
20

A 3 g sample of the acid-treated hydroxi-sodalite is kept in a Pt crucible for 3 hours at  $500^\circ\text{C}$  and it is checked if the material is fully amorphous. If the X-ray diffraction pattern of the material is not fully amorphous yet, the acid treatment of the hydroxi-sodalite will be repeated with 915 g of 5%  $\text{H}_2\text{SO}_4$  solution as per the  
25      procedure that has been described above and the crystal structure of the product of the acid treatment is checked again.

10.0 g of the dried amorphous intermediate product is subsequently wetted with 6.0 g of distilled water, 1 N NaOH solution is added to the blend until it gets  
30      slightly alkaline. Phenolphthalein indicator is used for this. The water content of

the NaOH solution (X g) is registered and later on it is to be deducted from the total amount of the water to be added when the synthesis slurry is composed.

8.5 g NaOH is dissolved in (40.2-X) g distilled water, the resulting solution is  
5 blended with 2.2 g concentrated sodium aluminate. (100 g concentrated sodium aluminate contains 0.194 moles of  $\text{Al}_2\text{O}_3$ , 0.309 moles of  $\text{Na}_2\text{O}$  and 3.394 moles of water.) The resulting solution is added to the amorphous material obtained from the acid treatment, 0.5 g of NaA nuclei (which has already been blended with some drops of water and ground in a mortar) is added to the slurry. The resulting  
10 synthesis slurry is properly homogenised by mixing and subsequently it is placed into a teflon-lined autoclave which can be rotated around a horizontal shaft. The autoclave has a volume of 180 ml. Some 3-4 teflon balls are placed into the autoclave. The autoclave is sealed and the slurry is aged for 1 hour at 40 °C by rotating the autoclave at 60 rpm (rotation per minute). This equipment provides a  
15 mixing by rocking agitation. The temperature is subsequently increased to 88°C and the crystallization takes place in 1.5 hours, meanwhile the mixing is continued.

The autoclave is subsequently cooled, the teflon balls are removed and the  
20 resulting slurry is poured into 200 ml of distilled water, subsequently filtered and the solids are washed with hot distilled water until the wash-filtrate's pH decreases to a value of 10. The product is dried at a temperature of 110°C. 13.4 g zeolite product of excellent quality is obtained in this way. The product contains 96% of NaA(LTA) zeolite. The main contaminant is less than 4% hydroxi-sodalite.

25

### Example 2

#### Making NaA zeolite from desilication product of an alumina refinery

The raw material is desilication product with the formula of  $1.01\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1.73\text{SiO}_2 \cdot 0.21\text{SO}_3 \cdot 1.24\text{H}_2\text{O}$  originating from an alumina refinery  
30 where the soda-limestone sintering process was used. 100 g of the raw material is blended with 427 g of 10%  $\text{H}_2\text{SO}_4$  solution and is treated with the acid solution as

per Example 1. The treatment lasts for 3 hours at 60°C and subsequently the resulting slurry is filtered, the solid phase is washed once with distilled water and dried at 110°C.

- 5        10 g of the dried amorphous intermediate product is subsequently wetted with 10 g of distilled water, and 1 N NaOH solution is added to the blend until it gets slightly alkaline. Phenolphthalein indicator is used for this. The water content of the NaOH solution (X g) is registered.
- 10       8.5g NaOH is dissolved in (36.0-X) g distilled water; the resulting solution is blended with the slurry containing the amorphous intermediate product. The resulting slurry is homogenised with mixing and subsequently it is placed into a teflon-lined autoclave that can be rotated around a horizontal shaft. Some 3-4 teflon balls are placed into the autoclave, the autoclave is sealed and the slurry is
- 15       aged for 3 hours at 40 °C by rotating the pot at 60 rpm. The temperature is subsequently increased to 88 °C and the crystallization takes place in 1.5 hours, meanwhile the mixing is continued.

- After such crystallization, the product is obtained as per the Example 1. The
- 20       amount of the product is 10.3 g well-crystallized NaA(LTA) zeolite as per its X-ray diffractometry pattern, with the presence of less than 2% of a hydroxi-sodalite contaminant.

### Example 3

- 25       **Making NaP<sub>6</sub> zeolite from hydroxi-sodalite**

- 100.0 g hydroxi-sodalite is treated with 5% H<sub>2</sub>SO<sub>4</sub> solution as per Example 1.
- 30.0 g of the dried amorphous intermediate product is subsequently wetted with 17.0 g of distilled water, and 1 N NaOH solution is added to the blend until it gets slightly alkaline. Phenolphthalein indicator is used for this. The water content of
- 30       the NaOH solution (X g) is registered.



7.5 g water glass of commercial grade is dissolved in (86.0-X) g distilled water. 100 g of water glass contains 0.443 moles of  $\text{SiO}_2$ , 0.192 moles of  $\text{Na}_2\text{O}$  and 3.633 moles of water. 17.4 g of solid NaOH is added to the water glass solution. The resulting solution is blended with the suspension of the amorphous intermediate product. 3.0 g of  $\text{NaP}_6$  nuclei are mixed with some drops of water, ground in a mortar and added to the slurry. The resulting slurry is homogenised with a shaking machine for 1.5 hours; subsequently it is placed into a teflon-lined autoclave. Some 3-4 teflon balls are placed into the autoclave. The autoclave is sealed, the temperature is subsequently increased to  $110^\circ\text{C}$  and the crystallization takes place in 4 hours under continuous mixing.

The amount of the product is 40.0 g well crystallized  $\text{NaP}_6(\text{GIS})$  zeolite as per its X-ray diffractometry pattern. The composition of the product corresponds to the formula  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2.3\text{SiO}_2 \cdot 2.5\text{-}3\text{H}_2\text{O}$ . Maximum 5% of hydroxi-sodalite is in the product as contaminant.

#### Example 4

##### Making $\text{NaP}_6$ nuclei

13.5 g solid NaOH is dissolved in 393 g of distilled water. The resulting solution is split into 2 parts so that one part is blended with 105.4 g of commercial grade water glass and the other part is blended with 51.5 g of concentrated sodium aluminate. The resulting solutions should be of nearly equal volume. 100 g of water glass contains 0.443 moles of  $\text{SiO}_2$ , 0.192 moles of  $\text{Na}_2\text{O}$  and 3.633 moles of water. 100 g of concentrated sodium aluminate contains 0.194 moles of  $\text{Al}_2\text{O}_3$ , 0.309 moles of  $\text{Na}_2\text{O}$  and 3.394 moles of water.

The solutions are cooled to  $+4^\circ\text{C}$  in a refrigerator, and the sodium aluminate solution is added to the sodium silicate solution within 2 minutes, meanwhile the latter is vigorously agitated. 17.4 g solid potassium perchlorate is added to the gel obtained by this way, and the mixing is continued for 0.5 hours so that the salt is dissolved.

The slurry is crystallized for 5 hours at 100°C and an rpm of 100/min. Rotating type mixing is applied in a teflon-lined autoclave that can be rotated around a horizontal shaft. Some 3-4 teflon balls are placed into the crystallizer autoclave. The temperature is subsequently increased to 110 °C and the slurry is crystallized for 1.5 hours meanwhile the mixing is continued.

The product is well-crystallized NaP<sub>e</sub> zeolite nuclei suspension as per its X-ray diffractometry pattern. The size of the crystals is less than 1 µm. This solid phase is difficult to filter; however, it can be used for the crystallization of a low Si/Al module NaP<sub>e</sub> zeolite without grinding.

#### Example 5

##### Making NaP<sub>e</sub> zeolite from desilication product of an alumina refinery

The raw material is desilication product (DSP) from an alumina refinery where bauxite is processed by the sintering method. The composition of the desilication product is the same as in Example 2. 100 g of DSP is treated with 5% sulfuric acid solution as described in Example 1. The slightly acidic amorphous intermediate product is filtered off, subsequently washed once with distilled water and subsequently dried at 110°C. 10 g of dried amorphous intermediate product is subsequently wetted with 10 g of distilled water, and 1 N NaOH solution is added to the blend until it gets slightly alkaline. Phenolphthalein is used for the indication of the alkalinity. The water content of the NaOH solution (X g) is registered.

6.0g solid NaOH is dissolved in (83.0-X) g distilled water. The resulting solution is blended with 2.0g water glass of commercial grade. 100 g of water glass contains 0.443 moles of SiO<sub>2</sub>, 0.192 moles of Na<sub>2</sub>O and 3.633 moles of water. The solution obtained in this way is blended with the suspension that contains the amorphous intermediate product. 1 g of NaP<sub>e</sub> nuclei is also added to the slurry after its mixing with some drops of water.

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The resulting slurry is homogenised in a shaking machine with the help of steel balls and subsequently it is placed into a teflon-lined autoclave. Some 3-4 teflon balls are placed into the crystallizer autoclave. The autoclave is sealed, the temperature is subsequently increased to 110°C and the crystallization takes place for 4 hours under continuous mixing. The temperature is subsequently increased to 135°C and the crystallization takes place for 2 hours under continuous mixing. The product is subsequently obtained as described in Example 1.

10 The amount of the product is 11.0 g well crystallized NaP<sub>6</sub>(GIS) zeolite as per its X-ray diffractometry pattern. The composition of the product corresponds to the formula Na<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.2.18SiO<sub>2</sub>.2.5-3H<sub>2</sub>O. Less than 3% of hydroxi-sodalite is in the product as contaminant.

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Claims:

1. A process for production of zeolites from raw materials with alkali alumino-hydrosilicate content comprising converting the alkali alumino-hydrosilicate content of the raw material into an amorphous state by acidic treatment, separating the intermediate amorphous solid material from the liquid phase and optionally purifying same, re-suspending it in water, alkalizing the suspension, followed by forming a slurry of the composition corresponding to the type of zeolite to be manufactured optionally by blending it with components containing  $\text{SiO}_2$ , and/or  $\text{Al}_2\text{O}_3$  and/or  $\text{Na}_2\text{O}$ , followed by crystallization by method known per se after optionally adding crystal nuclei and/or aging of the synthesis slurry and separating the obtained zeolite product.
2. The process according to Claim 1, wherein desilication product or alkali alumino-hydrosilicate containing scalings from an alumina manufacturing process is used as raw material.
3. The process according to Claim 1, wherein the amount of the acid that is needed for converting the alkali alumino-hydrosilicate to an amorphous state is determined by an experimental method, the evaluation of the X-ray diffractometry patterns of the samples.
4. The process according to Claim 1, wherein acidic waste from alumina refineries is used for the acidic treatment, which may contain solids and/or silica-containing scalings in solid and/or dissolved state.
5. The process according to Claim 1, wherein a mineral acid, preferably sulfuric acid is used for the acidic treatment.
6. The process according to Claim 5, wherein a diluted acid solution, preferably sulfuric acid solution of 3-60w% is used for the acidic treatment.
7. The process according to Claim 1, wherein the acidic treatment is carried out at 20-160 °C, preferably at 60-80 °C.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/HU 98/00094

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B39/02 C01B39/14 C01B39/46

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CA 1 004 655 A (INDUSMIN LTD) 1 February 1977 see claims 1-20 see page 5, column 3 - column 13 ---	1,7
A	KASAI TOSHIHIRO ET AL: "Waste materials utilization of red mud from Bayer process, recovery of rare metals and zeolite-synthesis" PROCEEDINGS OF THE 1ST INTERNATIONAL CONFERENCE ON PROCESSING MATERIALS FOR PROPERTIES; HONOLULU, HI, USA NOV 7-10 1993, 1993, pages 165-168, XP002092540 Warrendale, PA, USA see the whole document ----- -/--	1,7

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/HU 98/00094

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GID ROACH ET AL: "ZEOLITE PRODUCTION FROM DSP IN RED MUD FEEDSTOCK" LIGHT METALS, DENVER, FEB. 21 - 25, 1993, no. MEETING 122, 21 February 1993, pages 51-57, XP000379778 SUBODH K DAS ----	1,7
A	DATABASE WPI Section Ch, Week 8651 Derwent Publications Ltd., London, GB; Class E33, AN 86-338210 XP002091762 & SU 1 230 995 A (PHYS ORG CHEM INST) , 15 May 1986 see abstract ----	1
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A	CHEMICAL ABSTRACTS, vol. 110, no. 24, 12 June 1989 Columbus, Ohio, US; abstract no. 215764, SUDO KINGO: "Red mud treatment" XP002091761 see abstract & JP 63 286526 A24 November 1988 ----	1
A	WO 91 15427 A (ALCAN INT LTD) 17 October 1991 cited in the application see the whole document ----	1
A	DE 16 67 543 A (HERRMANN GEBR) 27 April 1972 see claim 1 see page 2, line 26 - page 3, line 34 -----	1

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Information on patent family members

International Application No

PCT/HU 98/00094

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